ABSORPTION STUDIES OF CHARGED EXCITATIONS IN α-SEXITHIOPHENE

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ABSTRACT

We present photoexcitation studies of vacuum deposited neutral films of α,ω-substituted sexithiophene (α-6T) using photoinduced absorption (PA) and PA-detected magnetic resonance spectroscopy (PADMR). We find evidence for photoinduced polarons having spin 1/2, with two absorption bands at 0.80 and 1.54 eV, respectively, and with negative PADMR signal at g ≈2. Similar absorption bands are observed in lightly p-doped sexithiophene and are interpreted as due to $6T^{\bullet+}$ radical cations. In addition, a PA band is found at 1.1 eV, which is shorter lived and decreases faster with increasing temperature than the polaron bands. As similar dication bands ($6T^{2+}$) have been found in heavily-doped α-6T, we identify this band as due to spinless bipolarons. Evidence of charge conjugation symmetry breaking in α-6T is presented. Finally, we have identified triplet excitons with triplet-triplet transition energy at about 1.45 eV.

INTRODUCTION

The novel optical and electronic properties of conjugated polymers, together with the promise of device applications, have stimulated considerable studies of these materials. Unlike traditional inorganic semiconductors, the physical and spectroscopic properties *strongly* depend upon preparation methods. Chemical and morphological defects such a chain twists can break the electronic conjugation, giving rise to a distribution of conjugation lengths. Oligothiophenes have drawn much interest,[1-4] because they possess well-defined conjugations lengths in addition to high purity. Hence, these materials can serve as model compounds for understanding the properties of polythiophene and other conjugated polymers. Furthermore, sexithiophene has shown promise of its own accord for applications such as organic field-effect transistors[5-6] and optical signal processing.[7]

In this work, we report studies of the spin nature of photoexcitations in α,ω-substituted sexithiophene (α-6T). As predicted by energy level calculations based on the nonempirical valence Hamiltonian technique,[8-9] polarons are characterized by two electronic transitions, whereas bipolarons have a single dominant transition. Doped sexithiophene (6T)[10-11] has been shown to support both spin-1/2 defects (radical cations and anions) and spinless bipolaron-like defects (dications or dianions). We have found, however, that the lower-energy polaron transition and the bipolaron transition in photoinduced absorption (PA) occur at different energies for positive and negative charges, proof of charge conjugation symmetry violation in α-6T. We are able to identify distinct spin signatures for polarons and bipolarons through comparison of the PA and PADMR spectra. We also report the absorption spectrum of triplet excitons at temperatures below 10K. The temperature, laser intensity, and modulation frequency dependencies could be satisfactorily explained by assuming that polarons and bipolarons are bound to shallow traps and their recombination are primarily monomolecular.

EXPERIMENTAL TECHNIQUE

The photoinduced absorption (PA) spectroscopy uses standard phase-sensitive lock-in techniques with a modulated Ar^+ laser beam as a source. Photoinduced changes ΔT in the sample transmission T are recorded to obtain the normalized changes in transmission ($\Delta T / T \approx \Delta\alpha d$, where d is the sample thickness). The PADMR technique uses a cw pump beam and a probe beam (from a tungsten lamp) to constantly illuminate the sample, which is mounted in a high Q microwave cavity (at 3 GHz) equipped with optical windows, and a superconducting magnet producing a field H. Microwave resonant absorption, which are nominally modulated at 800 Hz, leading to small change, δT, in the probe transmission. This δT is proportional to δn, the change in the photoexcitation density n produced by the Ar^+ pump beam. δn is induced by transitions in the microwave frequency range that change spin-dependent recombination rates. Two types of PADMR spectra are obtained: the H-PADMR spectrum, in which δT is measured at a fixed wavelength λ, and the λ-PADMR spectrum, in which δT is measured at a constant H, in resonance, while λ(probe) is varied.

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectrum of α-6T in CH_2Cl_2 doped with $FeCl_3^-$. The spectrum of the lightly-doped sample consists of two absorption bands P_1 and P_2, which are characteristic of $6T^{\bullet+}$ radical cations (or polarons). As the doping increases, these two bands decrease in intensity and a peak appears at midgap due to $6T^{2+}$ radical dications (bipolarons). At very high doping, the two polaron transitions vanish and the only remaining absorption bands are those of the bipolaron and a transition at 2.3 eV whose origin is not clear. These results are consistent with those of ESR studies,[12-16] which have reported a sharp increase in spin density for light doping followed by a decline at higher doping. As seen below, the absorption spectra of photoexcitations closely resemble the doping-induced absorption spectra.

The in-phase and out-of-phase PA spectra of α-6T measured at 10K with a modulation frequency of 200 Hz are shown in Figs. 2a and 2b. The spectrum exhibits three bands at 0.80, 1.1 and 1.54 eV, resp., accompanied by high-energy phonon replica at 0.97, 1.27, and 1.7 eV, resp. The bleaching of the in-phase PA above 1.7 eV is due to thermal modulation of the PL due to thermal heating by the probe. The relative positions of the PA bands correspond to the doping-induced bands shown in Fig. 1b. Hence, the bands at 0.8 and 1.54 eV are due to polarons and labelled P_1 and P_2; the band at 1.1 eV is due to bipolarons and labelled BP_1. As can be seen in Fig. 3b, BP_1almost completely disappears in the out of phase spectrum, proving that bipolarons are much shorter lived than polarons at 80K. Also, while BP_1 disappears above 110K, the polaron bands P_1 and P_2 are still visible at 300K.[17] We note the presence of a shoulder on the low energy side of P_1 as well as the fact that the feature at ≈1 eV is too strong to be solely due to a high-energy phonon sideband of P_1. The absence of such a strong sideband at ≈1 eV in the out of phase spectrum leads us to conclude that there is a substantial contribution from bipolarons in the in phase spectrum at 1 eV. These data are all manifestations of the differences between positive and negative photoexcitations, i.e., charge conjugation symmetry violation.

We can correlate the absorption spectra of photoexcitations with their spin states via the technique of PADMR. The H-PADMR spectrum, shown in Fig. 3a, includes both a narrow resonance at g≈2 due to spin-1/2 polarons and a half-field (Δm_S=2) resonance due to spin-1 triplet excitons. The λ-PADMR of the triplet excitons, shown in Fig. 3b, consists of a single, broad band centered with a double-peak at 1.4 and 1.55 eV, resp. In contrast, the spin-1/2 λ-PADMR contains both PA-quenching and PA-enhancing features. The two sharp negative PADMR bands coincide in energy with the two polaron PA bands P_1 and P_2. This is consistent with these two bands being due to spin-1/2 polarons and further indicates that magnetic resonance reduces the steady-state population of polarons. The presence of a broad, PA-enhancing PADMR between 1.0 and 1.45 eV suggests that magnetic resonance results in higher populations of bipolarons. In order to explain this result, we consider bipolaron generation and recombination processes:

Generation: $$P^{\pm} + P^{\pm} \rightarrow BP^{\pm\pm} \quad (1)$$

Recombination: $$BP^{\pm\pm} + P^{\mp} \rightarrow P^{\pm} \quad (2)$$

$$BP^{\pm\pm} + BP^{\mp\mp} \rightarrow S_0 \quad (3)$$

where S_0 is the ground state. As bipolarons are spinless, they can be formed only from like-charged polarons with antiparallel spins. Hence, this is a spin-dependent process which may be enhanced by magnetic resonance. While the recombination processes in Eqns. (2) and (3) are not spin-dependent, magnetic resonance reduces polaron populations which will in turn reduce the bipolaron recombination rate. Therefore, magnetic resonance results in increased bipolaron populations by either increasing their generation rate or reducing the recombination rate. The high-energy phonon sideband to the P_1 peak is not visible as it is canceled by an opposite contribution from bipolarons.

The long time dynamics of the photoexcitations can be studied by measuring the dependence of the PA and PADMR on the pump modulation frequency, temperature, and pump intensity, respectively. In Fig. 4, we show a set of PA spectra in the probe energy range 0.7-1.2 eV, taken at various pump modulation frequencies at 85K. It is clearly seen that the polaron peak at 0.8 eV and its shoulder at 0.96 eV behave differently than the bipolaron peak at 1.08 eV. In a previous report,[8] we have analyzed the P_1 frequency dependence and showed that it can be understood by assuming a wide distribution of lifetimes for the photoexcited polarons. We have recently reported the temperature dependence of the PA in 6T.[18] The behavior of the PA with temperature can be explained assuming an activation process for the lifetime τ of the form $\tau^{-1} = \tau_0^{-1} + \nu e^{-\Delta/k_B T}$, where Δ is the activation energy and τ_0 and ν are adjustable parameters. Following our analysis, we have found $\Delta = 50\, meV$ for the 0.80 and 0.96 eV polaron peaks and $\Delta = 32\, meV$ for the 1.08 eV bipolaron peak. These results indicate that polarons are more deeply trapped than bipolarons, giving rise to very different temperature dependence.

The dependence of the PA on the pump intensity I_L is shown in Figure 5. At low intensities $(I_L \leq 70mW/cm^2)$, the PA increases approximately as $I_L^{0.6}$ and saturates at higher intensities. In order to account for the intensity dependence over the whole intensity range, we assume a simple model in which the long lived photogenerated charges are bound to traps. As the pump intensity increases, the traps are filled, reducing the efficiency of producing these charges. We describe such a process by the following rate equation:

$$\frac{dn}{dt} = gI_L\left(1-\frac{n}{n_0}\right)-\frac{n}{\tau} \qquad (4)$$

where n is the density of trapped polarons and gI_L the rate at which photogenerated polarons are bound to free traps with density n_0. In this model, the factor $(1-n/n_0)$ in Eqn. (4) accounts for saturation, with n_0 being sample dependent. The steady state solution to Eqn. (4) is:

$$n = \frac{gI_L\tau n_0}{n_0 + gI_L\tau} \qquad (5)$$

The fit of Eqn. 5 to the data, shown as a dotted line in Fig. 5, is quite good. An attempt to fit the above data with a bimolecular recombination mechanism was not successful. The good fit obtained indicates that monomolecular recombination combined with "saturable generation" is a reasonable model.

SUMMARY

We have experimentally demonstrated, using PA and PADMR techniques, the existence of photogeneration polarons with spin-1/2, spinless bipolarons, and triplet excitons in α-6T. The polaron absorption spectrum consists of two transitions, whereas the bipolaron absorption spectrum is dominated by a single transition. The temperature, laser intensity, and modulation frequency dependencies could be satisfactorily explained by assuming that polarons and bipolarons are bound to shallow traps, where the dominant recombination process is monomolecular.

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[1]F. Garnier, in "Conjugated Polymers and Related Materials", Proceedings of the 81st Nobel Symposium, Edited by W. R. Salaneck, I. Lundström and B. Rånby; (Oxford University Press, 1993).

[2]M. Deussen and H. Bässler, Synthetic Metals **54**, 49 (1993)

[3]N. Periasamy, R. Danieli, G. Ruani, R. Zamboni, and C. Taliani, Phys. Rev. Lett. **68**, 2359 (1992)

[4]R. Zamboni, N. Periasamy, G. Ruani and C. Taliani, Synthetic Metals **54**, 57 (1993)

[5]A. Dodabalapur, L. Torsi, and H. E. Katz, *Science* **268**, 270 (1995)

[6]F. Garnier, G. Horowitz, X. Z. Peng and D. Fichou, *Adv. Mater.* **2**, 592 (1990)

[7]D. Fichou, J.-M. Nunzi, F. Charra, and N. Pfeffer, *Adv. Mater.* **6**, 64 (1994)

[8]J. Poplawski, E. Ehrenfreund, J. Cornil, J. L. Brédas, R. Pugh, M. Ibrahim, and A. J. Frank, Mol. Cryst. Liq. Cryst. **256**, 407 (1994)

[9]J. Cornil and J. L. Brédas, Adv. Mater. **7**, 295 (1995)

[10]D. Fichou, G. Horowitz, B. Xu and F. Garnier, *Synth. Met.* **39**, 243 (1990)

[11]P. Bäuerle, U. Segelbacher, K.-U. Gaudl, D.Huttenlocher and M.Mehring, Angew. Chem. (Eng.) **32**, 76 (1993).

[12]S. W. Sun and A. J. Frank, *J. Chem. Phys.* **94**, 4660 (1991)

[13]M. G. Hill, J.-F. Penneau, B. Zinger, K. R. Mann, and L. L. Miller, *Chem. Mater.* **4**, 1106 (1992)

[14]M. G. Hill, K. R. Mann, L. L. Miller, and J.-F. Penneau, *J. Am. Chem. Soc.* **114**, 2728 (1992)

[15]G. Horowitz, A. Yasser, and H. J. van Bardeleben, *Synth. Met.* **62**, 245 (1994)

[16]K. Tanaka, Y. Matsuura, Y. Oshina, T. Yamabe, and S. Hutta, *Synth. Met.* **66**, 295 (1994)

[17]P. A. Lane, X. Wei, and Z. V. Vardeny, unpublished results

[18]J. Poplawski, E. Ehrenfreund, J. Cornil, J. L. Brédas, R. Pugh, M.Ibrahim and A. J. Frank, Synthetic Metals **69**, 401 (1995)

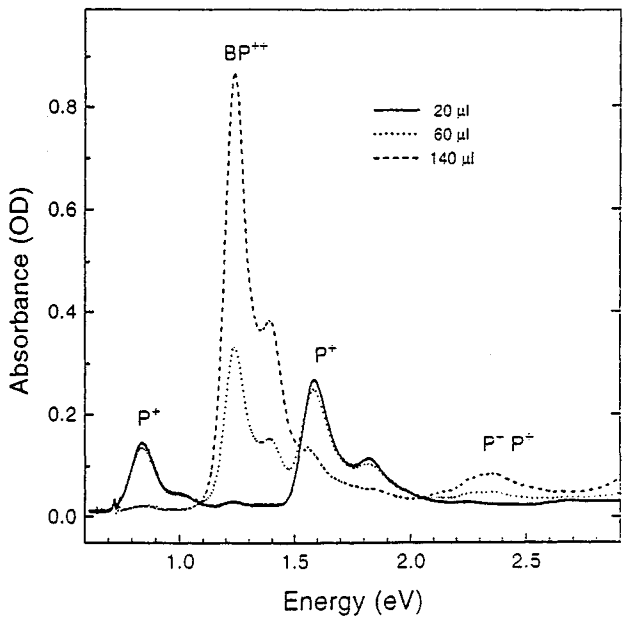

Figure 1. The absorption spectra of α-6T in CH_2Cl_2 doped with $FeCl_3^-$.

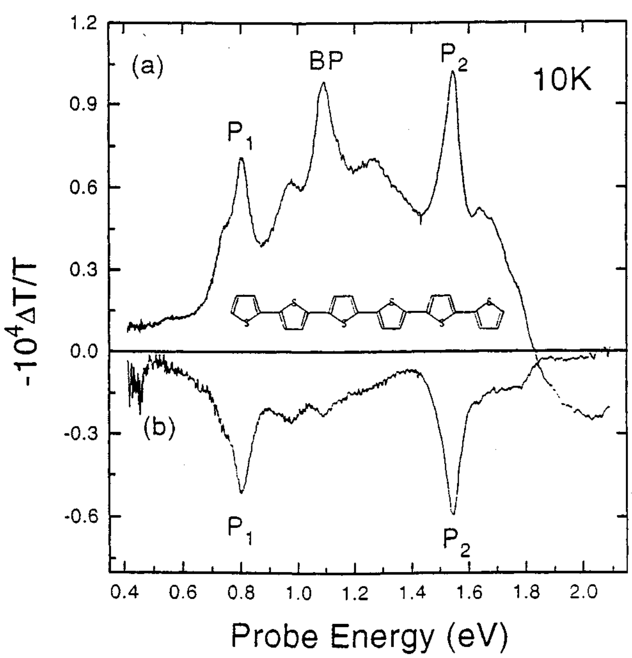

Figure 2. (a) In phase and (b) out of phase PA spectra of α-6T film at 10K. Inset: chemical structure of α-6T.

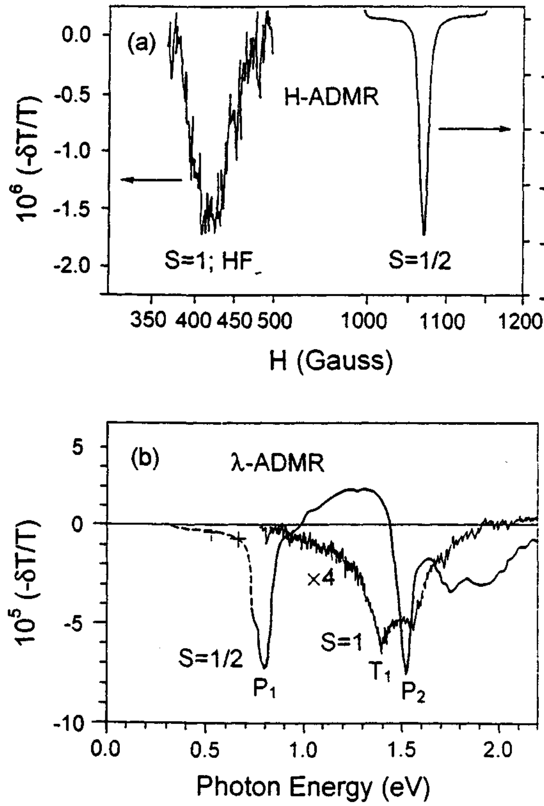

Figure 3. (a) H-PADMR and (b) λ-PADMR spectra of α-6T film below 10K.

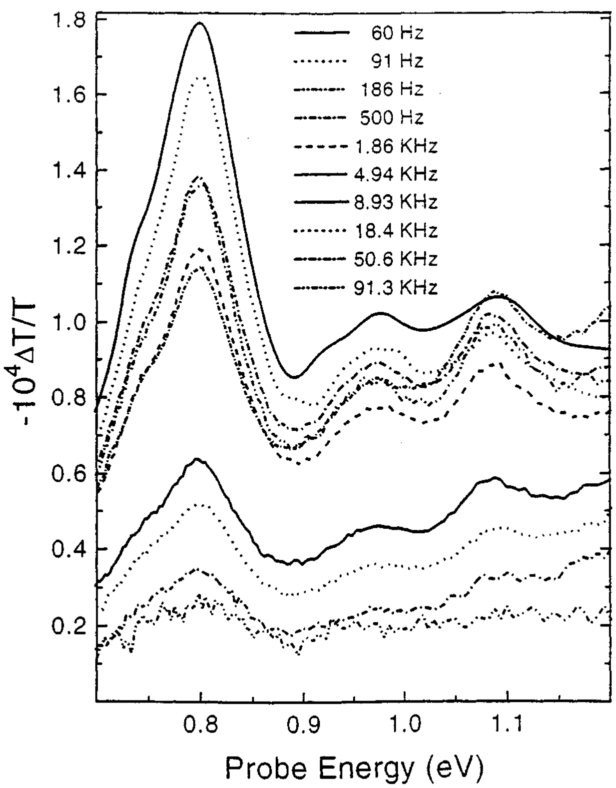

Figure 4. PA spectra of α-6T between 0.7 and 1.2 eV with modulation frequencies between 60 Hz and 91.3 kHz.

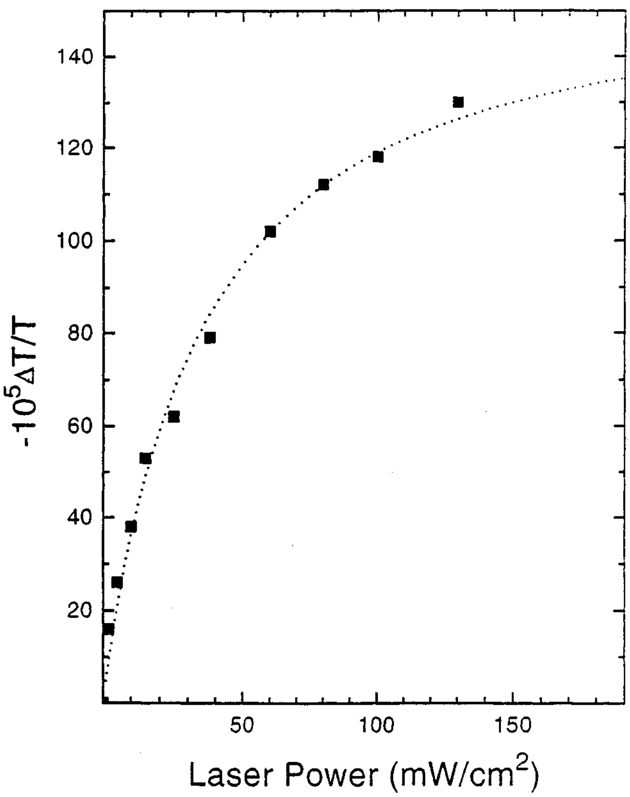

Figure 5. Dependence of the polaron PA vs. laser intensity.